EXHIBIT 23

THE ORIGIN OF THE VERMICULITE DEPOSIT AT LIBBY, MONTANA

WILLIAM A. BASSETT, *Columbia University, New York, N. Y.*

ABSTRACT

The country's largest vermiculite mine at Libby, Montana has been studied and the origin of the vermiculite deposit investigated. The ore body lies in an augite pyroxenite, which has been altered to biotite, hydrobiotite, and vermiculite. Numerous syenite dikes may be observed in the pyroxenite.

Ion exchange experiments show that biotite alters to vermiculate at room temperature in solutions of 0.001 molar magnesium or calcium chloride. Roy and Romo's evidence for the instability of vermiculite under hydrothermal conditions and its application to the origin of the vermiculite deposit at Libby, Montana is discussed. A mechanism is suggested for the formation of hydrobiotite, a regularly interstratified biotite-vermiculite.

It is concluded that augite altered to biotite at the time of the intrusion of the syenite dikes, and that the biotite was altered to hydrobiotite and vermiculite by supergene solutions.

INTRODUCTION

Vermiculite deposits of non-sedimentary origin are widely recognized, and many of them are similar in certain aspects. Vermiculite occurs as an alteration product of mafic minerals in an ultramafic body which has been intruded by small dikes and sills of acidic rock, usually pegmatites. The vermiculite usually occurs in fractures, along contacts of the ultramafic body with the country rock and along contacts between the ultramafic rock and the acid rock. It is accompanied by other alteration minerals such as antigorite, chrysotile, chlorite, talc, pyrophyllite, biotite, and amphiboles.

Vermiculite occurrences have been attributed both to hydrothermal and to supergene origins by different workers. Kulp (1954), in his study of the Day Book Dunite of Yancey County, North Carolina, attributed vermiculite to the supergene alteration of phlogopite. Hadley (1949) concluded that the vermiculite at Buck Creek, Clay County, North Carolina was the direct consequence of the intrusion of the pegmatite. Hagner (1944) studied the Wyoming vermiculite deposits and found evidence for the hydrothermal origin of the vermiculite. Thus, the origin of vermiculite deposits formed in seemingly similar environments has received different interpretations.

Libby, Montana is petrologically and mineralogically one of the simplest of the vermiculite deposits. Three sheet silicate minerals, biotite, hydrobiotite, and vermiculite, are involved. The original ultramafic was nearly a single mineral, augite, and the intruding acid rock, a syenite, is of simple composition. The simplicity of the mineral relationship has made it possible to study each chemical change and mechanism involved in the formation of the vermiculite deposit.

Case 2:17-cv-00063-D   Document 63-23   Filed 05/21   of 18

The term *vermiculite* in this paper refers to the mineral as defined by x-ray, optical, and chemical properties (Grim, 1953). The terms *vermiculite deposit* and *"vermiculite"* refer to the material of commercial interest which generally contains biotite and hydrobiotite in addition to vermiculite.

The Mining Operation

The Zonolite Company operation, about seven miles northeast of Libby, Montana, is at present the largest vermiculite mine in the country. The mine is on a hill about 4,000 feet above sea level and 2,000 feet above the Kootenai River, which flows through the valley three miles from the mine.

The mine is a large open pit (Fig. 1) with ten benches and has been in operation since 1923. The ore is handled by power shovels and heavy trucks. Little blasting is necessary, since the ore is soft and can be worked directly by the shovels. One ton of waste is mined for each ton of ore, and approximately 1,200,000 tons of ore are processed each year in a mill located just below the mine. The mill produces about 140,000 tons of concentrate each year, employing both wet and dry processes. This concentrate is shipped to various distributing points throughout the country, where it is heated in furnaces to 2,000° F., causing expansion to as much as 20 times its original volume. In this form it is marketed for insulation and horticultural purposes. The early history of the operation is described by Kriegel (1940).

Geological Setting

The ore body is a pyroxenite which intruded the Belt Series sediments and was later altered. Pardee and Larsen (1929) describe the Belt Series
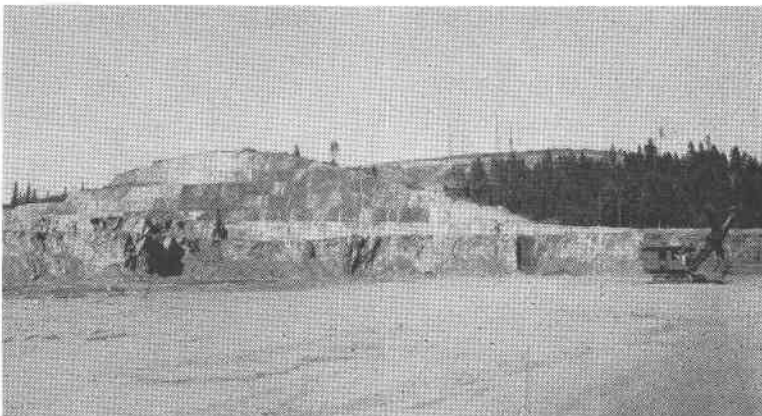

Fig. 1. The upper benches of the Zonolite mine at Libby, Montana.

in this area as argillites and quartzites which exhibit moderately steep dips and open folds that trend northwesterly. Near the borders of the pyroxenite, the argillites show metamorphism to hornstone which in places carries magnetite.

Pardee and Larsen's geologic map shows the pyroxenite as an irregularly shaped body about 3.5 miles long by 1.5 miles wide, with its long axis north-south. The original material was almost entirely augite, which was invaded by syenite dikes and subsequently altered to biotite, hydrobiotite, and vermiculite.

Southwest and adjacent to the pyroxenite is a syenite intrusive about two-thirds as large, which consists principally of potash and soda feldspars. Pardee and Larsen (1929) report hornblende, fluorite, apatite, sphene, rutile, biotite, and garnet as accessory and secondary minerals. A dike-like projection of the syenite extends into the pyroxenite. The syenite dikes which cut the pyroxenite range from a few inches to several feet in thickness (Fig. 2) and were probably fed by the major projection of the syenite.

Pyroxenite

The pyroxenite was probably originally an almost pure coarse-grained augite. Crystals as much as 3 inches long are easily discernible, even

FIG. 2. A typical syenite dike cutting the altered pyroxenite.

Fig. 3. Horizontally oriented crystals in the wall of the mine. The vertical marks
at the left were made by a power shovel.

though some of them are almost completely altered. The larger crystals
show a strong horizontal orientation (Fig. 3). At many points, domains
of horizontally oriented crystals are distinctly cut by domains of finer
grained augite showing vertical flow features. These domains of ver-
tical flow are particularly conspicuous because of their vertical banding
(Fig. 4).

New magma from below might have produced the vertical flow fea-
tures, but such a mechanism should produce grosser and more contin-
uous features rather than the small domains observed.

The contacts of the pyroxenite are characterized by a high concentra-
tion of magnetite and apatite. Where the pyroxenite is in contact with the
Belt sediments, augite, magnetite, and apatite have penetrated a short
distance into the metamorphosed sediments as dark fine-grained (1 mm.)
bands. In the pyroxenite, magnetite and apatite are more abundant near
the contact. Both minerals are fine-grained (5 mm.) and are dissemi-
nated in a relatively fine-grained augite. The apatite occurs as well crys-
tallized hexagonal prisms. Since the rock is friable because of the altera-
tion of the augite, the prisms readily separate. The magnetite-apatite
zone appears both along the pyroxenite-syenite contact and the pyroxe-
nite-sediment contact.

Syenite

The mine workings have exposed numerous thin syenite dikes, rang-
ing from a few inches to several feet thick, which cut the pyroxenite
(Fig. 2). The syenite consists of potash and soda feldspars intergrown as
perthites in some places and discrete in others. The ratio of soda to pot-
ash feldspar varies from point to point. The individual dikes almost cer-

FIG. 4. Vertical flow features in the pyroxenite. These probably represent later injections of augite magma. Thin asbestos veins cross diagonally.

tainly represent different introductions of magma separated by short intervals of time. Pardee and Larsen observed minor textural variations in the main body of syenite, which they attributed to separate introductions. In some places, the syenite is quite dark, due to the presence of finely disseminated hornblende crystals. The hornblende is probably not a product of the syenite magma but is the result of assimilation of augite by the syenite magma. Figure 5 shows crystals cutting across a syenite-pyroxenite contact. These crystals are augite at the end which extends into the pyroxenite and hornblende pseudomorphous after augite at the end which projects into the syenite.

Alteration Products of the Pyroxenite

Four alteration minerals predominate, asbestos (tremolite-actinolite), biotite, hydrobiotite, and vermiculite. The name hydrobiotite was applied by Gruner (1934) to interstratified biotite-vermiculite from Libby. This mineral, along with vermiculite and biotite, constitutes the commercial "vermiculite" ore.

Many thin (approximately 1 inch), white asbestos veins cut through the pyroxenite. The asbestos has been identified by x-ray diffraction and optically as tremolite-actinolite. It differs from augite in that it contains water and has a higher silica content. Some thick asbestos veins contain
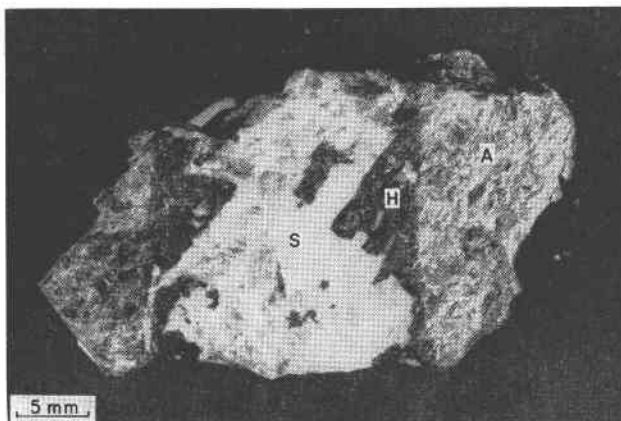
Fig. 5. A small syenite dike (S) which has altered projecting
augite crystals (A) to hornblende (H).

cores of quartz, which indicates that silica-rich solutions were probably
responsible for altering augite to tremolite-actinolite (Fig. 6). This quartz
is the only free silica found in the mine.

The asbestos is also found disseminated through the intrusive as thin
layers along cleavage planes of the augite. These tend to greatly exag-
gerate the cleavage, and as a result, complete crystals or even large
fragments of augite are almost impossible to find.

Biotite, hydrobiotite, and vermiculite are widely distributed general
alteration products of the augite. These minerals are also found along
cleavage planes of the augite (Fig. 7). Their orientation is derived from
the augite by this mechanism and remains even where no original augite
exists.

Unaltered patches of augite several feet across are found in the mine.
These appear to be domains which were not permeated by the altering
solutions. Similarly, there are patches of biotite which have not been
altered to hydrobiotite and vermiculite. This feature is the strongest
field evidence for the derivation of hydrobiotite and vermiculite from
biotite rather than from augite by hydrothermal action. The unaltered
biotite patches are quite separate from the augite patches, suggesting
that the alteration of augite to biotite and the alteration of biotite to
hydrobiotite and vermiculite occurred at different times.

Vermiculite differs from biotite in the composition of the intersilicate
layer. The intersilicate layer in biotite consists of potassium ions, while
the intersilicate layer in vermiculite consists of bivalent ions distributed
between two layers of water molecules. Alteration from biotite to ver-
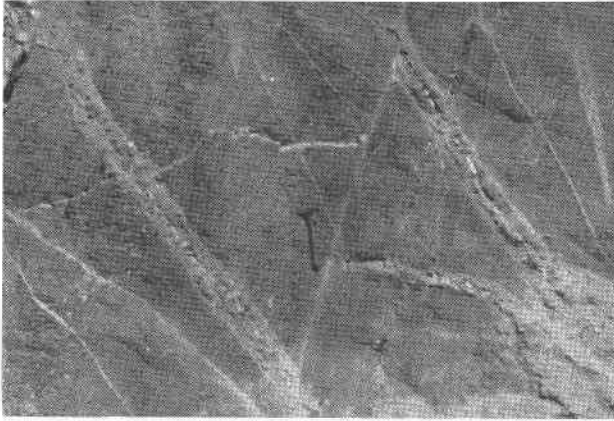miculite takes place when hydrated bivalent ions in solution replace the

FIG. 6. An offset asbestos vein showing a core of quartz.

potassium ions in biotite. In hydrobiotite, potassium intersilicate layers alternate with intersilicate layers containing bivalent ions and water molecules. An analysis by the Zonolite Company of the exchangeable cations reveals that the concentrate from Libby contains 20.8 milli-equivalents of calcium and 12.0 milli-equivalents of magnesium per hundred grams of concentrate. A complete analysis of the concentrate is given in Table 1 (Zonolite 1954).

An oriented sample of concentrate from the mill was run on the x-ray diffractometer (Fig. 8b). The resulting pattern indicates that biotite, hydrobiotite, and vermiculite are present in about equal amounts. Only about 1 per cent of the flakes in the concentrate, however, are discrete biotite and fail to exfoliate on ignition. In the commercial process, these unexpanded flakes are separated from the final product by air sorting.
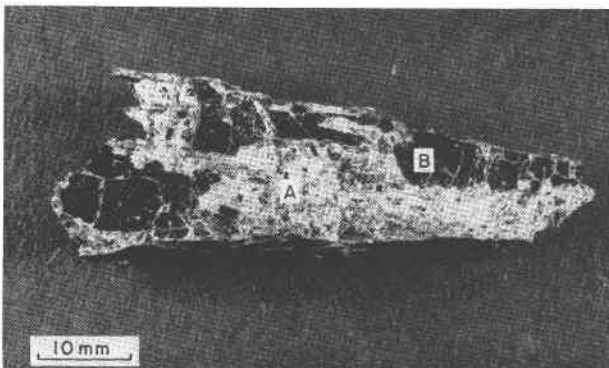

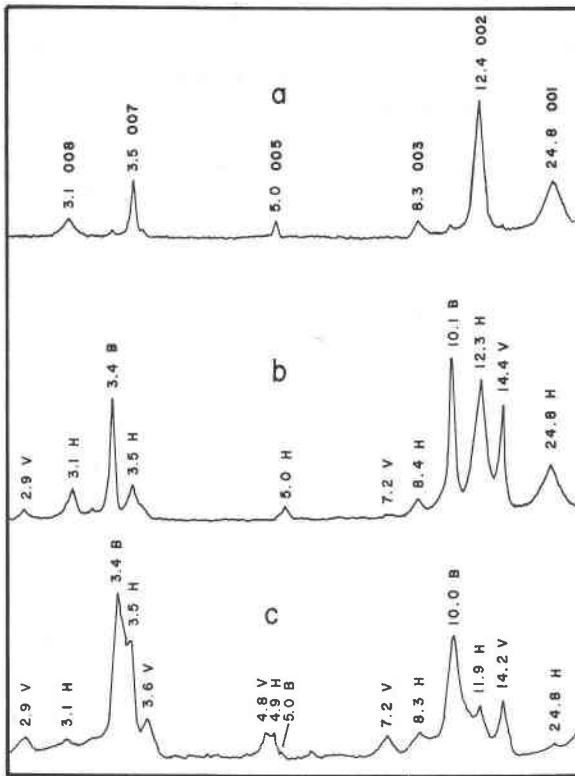FIG. 7. Augite (A) partially altered to biotite (B) along cleavage planes.

FIG. 8. X-ray diffraction data. (a) Hydrobiotite from the Zonolite mine at Libby, Montana. (b) Concentrate from the mill at Libby, Montana containing biotite (B), hydrobiotite (H), and vermiculite (V). (c) Copper hydrobiotite (H) and copper vermiculite (V) synthesized from biotite (B).

The biotite shown in the x-ray pattern is probably intimately mixed with the hydrobiotite and vermiculite.

Only hydrobiotite and vermiculite provide the water which is turned to steam in the exfoliation process. One might expect the biotite to act only as a diluent decreasing the yield of the expanded material. This is not the case, however, for the biotite compensates for its deficiency as a source of steam by providing strength to the layers and impeding the escape of steam produced by the hydrobiotite and vermiculite. The biotite interstratified with vermiculite in the hydrobiotite probably serves the same function.

A pure vermiculite from Corundum Hill, North Carolina, when ignited, shows a much greater tendency to decrepitate. Expanded concentrate from Libby placed in water and prepared for x-ray diffraction in

TABLE 1. CHEMICAL ANALYSIS OF CONCENTRATE FROM LIBBY (ZONOLITE, 1954)

SiO_2	38.64
MgO	22.68
Al_2O_3	14.94
Fe_2O_3	9.29
K_2O	7.84
CaO	1.23
Cr_2O_3	0.29
Mn_3O_4	0.11
P_2O_5	trace
S	trace
Cl	0.28
H_2O	5.29
Total	100.59

a Waring Blendor yields a biotite diffraction pattern. Expanded vermiculite from Corundum Hill prepared in the same way gives a diffraction pattern showing a 9.4 Å reflection resulting from the collapse of the vermiculite lattice after the interlayer water is driven out. It is of interest to note that biotite seems to be an essential constituent of commercial "vermiculite."

OPTICAL DATA

Both color and refractive index change as biotite alters to hydrobiotite and vermiculite (Table 2). The color of the unaltered biotite is gray-green, whereas the color of the hydrobiotite is light brown and vermiculite is neutral gray. These color differences are used by the miners in selecting ore and avoiding the domains of unaltered biotite. The refractive index and the birefringence decrease as the water content increases from biotite to hydrobiotite to vermiculite. The optic sign and the 2V remain unchanged.

The partial alteration of a flake of biotite to vermiculite is shown in

TABLE 2. OPTICAL DATA ON THE ORE MINERALS FROM LIBBY

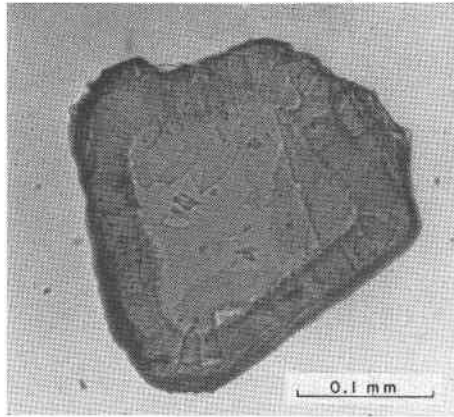| Mineral	Color	α	γ	$\gamma-\alpha$	Sign	2V
Biotite	Gray-green	1.570	1.610	0.040	$(-)$	0–5°
Hydrobiotite	Light brown	1.560	1.595	0.035	$(-)$	0–5°
Vermiculite formed synthetically from biotite	Neutral gray. Berlin blue under crossed nicols	1.530	1.555	0.025	$(-)$	0–5°

Fig. 9. A biotite flake which has been altered to vermiculite along the edges by immersion in a molar magnesium chloride solution at 100° C. for 6 hours.

Fig. 9. The biotite was placed in molar magnesium chloride at 100° C. for 6 hours. The change in refractive index shows clearly the penetration of the alteration into the flake. Under crossed nicols, the rim of vermiculite has an anomalous blue birefringence of the first order, similar to that found in penninite.

LABORATORY INVESTIGATIONS

Field observations at Libby, Montana suggest that hydrobiotite and vermiculite formed as alteration products of biotite which had previously been formed by the alteration of augite. Separate domains of unaltered biotite and unaltered augite suggest that there were two periods of alteration: soaking of the pyroxenite with alkali-silica rich hydrothermal solutions to produce biotite from the augite, and soaking of the pyroxenite, now partially altered to biotite, with magnesium-calcium rich solutions to produce hydrobiotite and vermiculite from the biotite. The depth to which the ore extends indicates that both of the altering solutions permeated the pyroxenite. Such extensive permeation suggests hydrothermal solutions; yet the high relief of the region could also permit deep penetration of the supergene solutions.

These field observations suggest some questions which might be resolved by laboratory experiments:

1. Under what conditions does biotite alter to vermiculite?
2. Is vermiculite stable under hydrothermal conditions?
3. What is the nature of the mixed layer structure observed in hydrobiotite and what conditions lead to its formation?

Alteration of Biotite to Vermiculite

Barshad (1948) conducted ion exchange experiments on vermiculite and biotite. He showed that vermiculite can be produced by placing biotite in a solution of neutral molar magnesium chloride at 70° C. for 10 days. The use of large samples (0.5–2.0 grams) made it necessary to change the solutions and wash the samples daily. He showed also that the vermiculite can be altered to biotite by placing it in a potassium solution.

The writer was able to confirm these results and extended the ion exchange experiments to include a greater variety of concentrations, temperatures, and reaction times (Table 3). The results indicate that the reaction proceeds under much less intense conditions than those used by Barshad. Some of the unaltered biotite from Libby altered partially to vermiculite in a 0.001 molar magnesium chloride solution in 56 hours at room temperature. It showed similar behavior in a calcium chloride solution of the same concentration.

The failure of the reaction to go to completion may be attributed to two conditions: (a) the inhibiting effect of potassium in the solution and (b) an inherent reluctance of some of the biotite to alter to vermiculite. Potassium is released into the solution from the biotite as the magnesium enters the biotite to replace the potassium. As the concentration of the potassium in the solution builds up, the alteration of the biotite becomes slower until equilibrium is reached and the reaction is halted. Under laboratory conditions, this point is characterized by the coexistence of discrete biotite and vermiculite. Under natural conditions of more dilute solutions, greater reaction times, and more dynamic conditions, the failure of the reaction to go to completion is believed to result in mixed-layer biotite-vermiculite. This is discussed in more detail later.

When 1 mg. of biotite from Libby was immersed in 50 ml. of 0.001 molar magnesium chloride, the biotite altered completely to vermiculite, while 50 mg. of biotite under similar treatment (Table 3) altered only partially to vermiculite. This confirms the importance of the inhibiting effect of the potassium released from the biotite.

The inhibiting effect of potassium is more pronounced when high concentrations are used. A molar solution of magnesium chloride containing 0.04 molar potassium chloride does not alter biotite to vermiculite. In more dilute solutions (0.001 molar), the potassium-magnesium ratio may be as high as 1:1 and still effect a partial alteration of biotite to vermiculite.

Two significant facts are brought out by the experiments described

TABLE 3. THE ARTIFICIAL ALTERATION OF BIOTITE TO VERMICU-
LITE UNDER VARIOUS CONDITIONS

Sample: Unaltered biotite from Libby, Montana
Quantity of Sample: 50 mg.
Sample Size: Smaller than 149 microns.
Quantity of Solution: 50 ml.

Composition of Solution	Temperature (degrees C.)	Number of Hours	Percentage Biotite Alteration to Vermiculite
0.2 molar $MgCl_2$	100	56	100
0.1 molar $MgCl_2$	100	56	95
0.01 molar $MgCl_2$	100	56	60
0.001 molar $MgCl_2$	100	56	35
1 molar $MgCl_2$	R.T.*	72	50
0.2 molar $MgCl_2$	R.T.	56	35
0.1 molar $MgCl_2$	R.T.	56	35
0.01 molar $MgCl_2$	R.T.	56	25
0.001 molar $MgCl_2$	R.T.	56	15
0.01 molar $CaCl_2$	100	24	45
0.001 molar $CaCl_2$	100	24	35
0.01 molar $CaCl_2$	R.T.	24	20
0.001 molar $CaCl_2$	R.T.	24	15
0.001 molar $CaCl_2$ 0.001 molar $MgCl_2$	100	24	40
0.001 molar $CaCl_2$ 0.001 molar $MgCl_2$	R.T.	48	15
1 molar $MgCl_2$ 0.02 molar KCl	100	48	30
1 molar $MgCl_2$ 0.03 molar KCl	100	48	10
1 molar $MgCl_2$ 0.04 molar KCl	100	48	<1
0.001 molar $MgCl_2$ 0.0001 molar KCl	100	48	70
0.001 molar Mg 0.001 molar KCl	100	48	40

* R.T.=room temperature.

above. The first is that biotite readily alters to vermiculite under conditions of very low concentrations, low temperatures, and short reaction times. The other is that when the potassium concentration in a solution exceeds 0.04 molar, biotite does not alter to vermiculite even when the magnesium concentration is molar and the temperature is 100° C.

The first of these facts shows that vermiculite can form from biotite

under supergene conditions. The second indicates that the solutions which produced the vermiculite were probably quite separate in time from the alkaline-rich solutions which must have accompanied the introduction of the syenite at Libby.

The Stability of Vermiculite under Hydrothermal Conditions

Roy and Romo (1957) subjected vermiculite to hydrothermal conditions in a bomb. They found that at 10,000 p.s.i. the vermiculite undergoes a change when it is heated above 200° C. Above 200° C., the 4.7 Å and 7.0 Å reflections on the x-ray diffraction patterns increase in intensity with respect to the 14 Å reflection. They suggest that a type of chlorite is formed, although the intensity relationships do not shift all the way to a chlorite pattern, but give a pattern representing some sort of mixture of vermiculite and chlorite. They suggest that magnesium ions migrate from the octahedral position of the vermiculite to the intersilicate position where they increase the scattering power of the intersilicate layer and decrease the scattering power of the octahedral layer to produce the changes observed in the x-ray pattern.

Roy and Romo show the DTA patterns of vermiculite before hydrothermal treatment and after hydrothermal treatment. The pattern of the vermiculite before the treatment has a pair of endothermic peaks in the range 100° C. to 300° C. The DTA pattern of the material after hydrothermal treatment shows a minor endothermic reaction at about 180° C. and a strong endothermic reaction at about 640° C.

Characteristically, vermiculite shows a pair of endothermic reactions between 100° C. and 300° C., due to the loss of H_2O from the intersilicate position. The low temperature peak is attributed to the loss of water molecules not in contact with the magnesium ions. The higher temperature endothermic peak results from the removal of the more tightly bound water molecules in contact with the magnesium ions (Mackenzie 1957, p. 194). Chlorite gives a DTA pattern with a strong endothermic reaction in the range 450° C. to 650° C. due to dehydroxylization of the brucite layer (Mackenzie 1957, p. 215).

The writer suggests a different interpretation from that offered by Roy and Romo for the changes taking place in the vermiculite when treated hydrothermally. The DTA diagrams indicate the presence of hydroxyl ions in the intersilicate position along with H_2O molecules rather than just H_2O molecules as shown in Roy and Romo's diagrams. The writer suggests that hydrolysis takes place in the bomb, providing the magnesium ions with hydroxyl ions in their hydration envelopes. Thus, more magnesium ions can be accommodated in the intersilicate position because some of the positive charge of the magnesium ions is balanced by

the hydroxyl ions. It would be interesting to know if vermiculite would alter to chlorite completely if more magnesium were made available.

Regardless of the interpretation, the data strongly suggest that vermiculite does not continue to *exist* as vermiculite under hydrothermal conditions (10,000 p.s.i. over 200° C.) and that it therefore could not *form* under hydrothermal conditions. The only reservation which the writer has in arriving at such a conclusion is that the acidity of the hydrothermal solution might have a pronounced effect on the temperature at which the transition from vermiculite to chlorite takes place if the transition is actually effected by hydrolysis. There is a need for more extensive experiments in this realm of investigation.

Hydrobiotite (mixed-layer biotite-vermiculite)

Gruner (1934) described a specimen from Libby, Montana which he found to be mixed-layer biotite-vermiculite and which he designated hydrobiotite, since it retains many of the characteristics of biotite and yet contains a large quantity of water.

Two types of mixed-layer structure exist, randomly interstratified and regularly interstratified. The randomly interstratified mixed-layer structure gives an irrational sequence of basal reflections on a diffractometer diagram. That is, the reflections cannot be indexed (001), (002), (003), etc. Instead, they occur between adjacent reflections of the component minerals. On the other hand, the regularly interstratified mixed-layer structure gives a rational sequence of reflections with a (001) reflection having a spacing which is the sum of the spacings of the components. The reflection for the sum of the spacings of the components may sometimes be observed in randomly interstratified mixed-layer structures (Weaver 1956, p. 217) but is generally broad.

Hydrobiotite from Libby, Montana was prepared in distilled water in a Waring Blendor for 5 minutes. The suspension was allowed to sit for a minute while the coarse fragments settled out. Then the fines (less than 50 microns) were transferred in suspension to a settling dish where they were sedimented onto a glass slide for 10 minutes. The water was then removed and the sample air dried.

Three samples of hydrobiotite from different parts of the mine were prepared in this way and run on the x-ray diffractometer immediately after preparation. The resulting patterns had rather broad reflections, with the most intense reflection at 11.5 Å, which were found to be in fair agreement with the values reported by Gruner (1934). The same samples, still mounted on the glass slides when rerun a month later, gave results (Fig. 8a) quite different from those obtained earlier. The reflections were sharp and the most intense reflection had shifted to 12.4 Å.

The change which took place is attributed to a change in the degree of hydration of the vermiculite layers in the hydrobiotite. The vermiculite layers in the original sample are probably partially and randomly hydrated. After grinding to a fine particle size and exposure to the air for a period of a month, the layers picked up water and expanded to the full 14 Å.

A fully hydrated sample gives a rational series of basal reflections indicating that it is regularly interstratified (Fig. 8a). The spacing represented by the (001) reflection is almost exactly the sum of the (001) spacings for the biotite (10 Å) and the vermiculite (14 Å) found at Libby, indicating that the ratio of biotite to vermiculite is 1:1 and almost certainly a sequence of BVBVBVBVBV.

The hydrobiotite occurs in the mine as domains several feet across in which there is almost no discrete biotite and vermiculite, as indicated by the diffraction pattern of hydrobiotite collected *in situ* (Fig. 8a). A sample of concentrate from the mill served as a representative blended sample of the micaceous minerals from a large portion of the mine. A diffraction pattern of this material (Fig. 8b) shows that hydrobiotite occurs in the same order of abundance as biotite and vermiculite in the mine. The sharpness of the hydrobiotite reflections indicates that there is no appreciable variation in the biotite to vermiculite ratio in the hydrobiobite, even when material is sampled from a large portion of the mine. The wide distribution of the 1:1 regularly interstratified biotite and vermiculite seems to indicate that this is a relatively stable configuration.

None of the ion exchange experiments involving the immersion of biotite in magnesium and calcium solutions yielded hydrobiotite. However, mixed-layer biotite-vermiculite has been produced experimentally in two ways: (a) by immersing 10 mg. of biotite in molar cupric chloride for 100 hours at 100° C. (Fig. 8c)* and (b) by immersing vermiculite in solutions of varying potassium concentrations. The former of these methods yielded a regularly interstratified 1:1 mixed-layer structure and has been designated copper hydrobiotite (Bassett, 1958).

The positions and intensities of the copper vermiculite reflections are different from those of magnesium and calcium vermiculite because hydroxyl ions accompany the copper in the intersilicate position. The latter method produced mixed-layer structures of varying ratios, depending on the concentration of the potassium, the temperature, and the reaction time. It showed no tendency to form a stable ratio as found in the natural hydrobiotite or the synthesized copper hydrobiotite. This suggests that the hydrobiotite found at Libby, Montana formed from the action of dilute magnesium and calcium solutions on biotite rather

---

* Copper hydrobiotite was synthesized during the investigation of copper bearing vermiculites from Northern Rhodesia.

than the action of potassium on vermiculite. The solutions which produced the natural hydrobiotite were probably even more dilute and required greater lengths of time than the most dilute solutions which altered biotite to vermiculite artificially.

It is possible that hydrobiotite formed as a result of slight fluctuations in the potassium to magnesium (and calcium) ratio of the altering solutions. Such fluctuations could result from fluctuations in flow and temperature of the solutions.

The following mechanism is offered as an explanation for the stability of the 1:1 regularly interstratified biotite-vermiculite:

Potassium binds the silicate layers together more tightly than hydrated magnesium or calcium because the bond length from the silicate sheet to the potassium ions in the biotite structure is shorter than the bond length from the silicate sheet to the magnesium or calcium ions in the vermiculite structure. If the potassium ions in a single layer of biotite are replaced by hydrated magnesium or calcium, then the bonding in that layer becomes weaker. As a result, the bonding in the adjacent layers which still contain potassium ions becomes stronger. The next layers of potassium ions to be replaced by hydrated magnesium or calcium are not the adjacent layers (because they are now more tightly bound) but the layers beyond the adjacent layers. When these are replaced by magnesium or calcium, the bonding is weakened and the potassium in the biotite layer, now sandwiched between two vermiculite layers, is even more tightly bound.

Conclusions

Hydrobiotite and vermiculite are believed to have formed by the supergene alteration of biotite:

1. The occurrence of domains of unaltered biotite spatially removed from domains of unaltered augite is evidence for two stages of alteration, one which produced biotite from augite and another which produced hydrobiotite and vermiculite from biotite.

2. Ion exchange experiments show that biotite readily alters to vermiculite in solutions of 0.001 molar concentration of magnesium and calcium at room temperature.

3. Ion exchange experiments show that when the potassium concentration of a solution exceeds 0.04 molar, biotite does not alter to vermiculite even when the magnesium concentration is molar and the temperature is 100° C.

4. Roy and Romo (1957) have conducted experiments which indicate that vermiculite partially alters to chlorite under hydrothermal conditions (10,000 p.s.i. and greater than 200° C.). The Libby vermiculite is not chloritic.

AUGITE
$(Ca,Mg)(Mg,Fe,Al)(Si,Al)_2O_6$

+K
+SiO_2
+OH

HYDROTHERMAL

+SiO_2
+OH

BIOTITE
$K(Mg,Fe)_3(OH)_2(Al Si_3)O_{10}$

TREMOLITE-ACTINOLITE
$Ca_2(Mg,Fe)_5(OH)_2(Si_4O_{11})_2$

+Mg
+Ca
-K

SUPERGENE

HYDROBIOTITE
$K(Mg,Fe)_3(OH)_2(Al Si_3)O_{10}$
$(Ca,Mg)_{0.5}(H_2O)_x(Mg,Fe)_3(OH)_2(Al Si_3)O_{10}$

+Mg
+Ca
-K

SUPERGENE

VERMICULITE
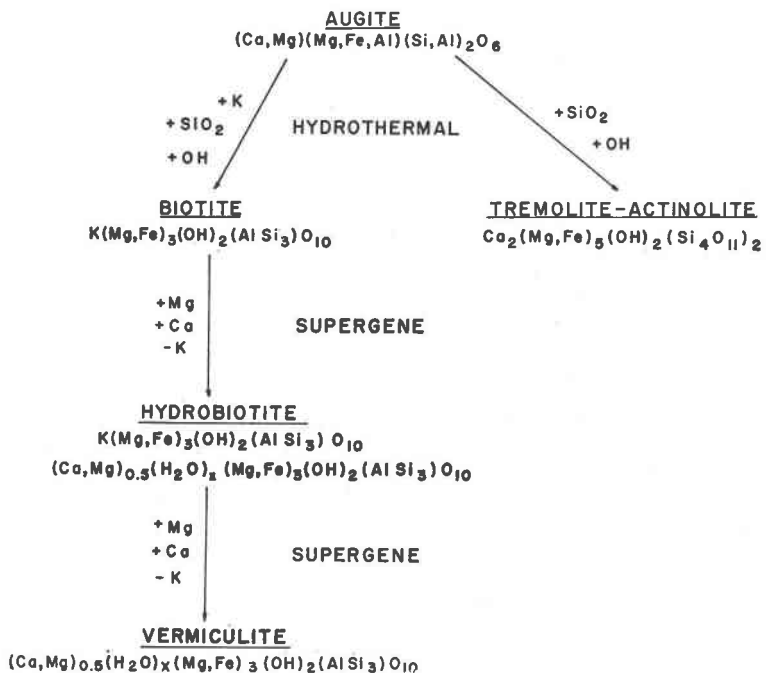$(Ca,Mg)_{0.5}(H_2O)_x(Mg,Fe)_3(OH)_2(Al Si_3)O_{10}$

FIG. 10. The chemical changes involved in the alteration of augite at Libby, Montana.

5. Hydrobiotite, a regularly interstratified biotite-vermiculite, has not been produced from biotite in the laboratory by immersion in magnesium and calcium solutions but has been produced by immersing biotite in a molar cupric chloride solution at 100° C. for 100 hours.

The sequence of events leading to the formation of the commercial deposit of "vermiculite" at Libby, Montana started with the intrusions of a pyroxenite magma into the Belt series sediments. Textural and structural features of the pyroxenite indicate that the magma was very fluid and formed a laccolith-like body. After the pyroxenite had solidified, syenite intruded the sediments to the southwest of the pyroxenite body and penetrated the pyroxenite in the form of numerous small dikes. The syenite probably intruded a short time after the pyroxenite and was genetically related to it. At the same time that the syenite dikes intruded the pyroxenite, hydrothermal solutions rich in silica and alkalis permeated the pyroxenite, altering the augite to tremolite-actinolite and biotite.

The next important event in the formation of the deposit was probably the elevation and dissection of the region. This permitted access of supergene solutions to the altered pyroxenite even at considerable depth.

As these solutions passed through the body, they picked up magnesium and calcium from the augite or from soluble calcium and magnesium minerals which formed from augite at the time it was altered to biotite and tremolite-actinolite. The magnesium and calcium then replaced the potassium in the intersilicate layers of the biotite, altering the biotite to hydrobiotite and vermiculite. Figure 10 is a graphic representation of the chemical changes involved in this sequence of events.

ACKNOWLEDGMENTS

The program was conducted at and supported by the mineralogical laboratory at Columbia University under the guidance of Professor Paul F. Kerr, who has provided advice and encouragement. The author is indebted to the Zonolite Company for permission to work in the mine at Libby, Montana and especially to Mr. Raymond Kujawa of Zonolite for many helpful observations. The author wishes to express his gratitude to Mr. Martin W. Molloy for his assistance in the field and to Dr. Davis M. Lapham for many stimulating discussions.

REFERENCES

BARSHAD, I. (1948), Vermiculite and its relation to biotite as revealed by base exchange reactions, x-ray analyses, differential thermal curves, and water content: *Am. Mineral.*, **33**, 655–678.

BASSETT, W. A. (1958), Copper Vermiculites from Northern Rhodesia: *Am. Mineral.*, **43**, 1112–1133.

GRIM, R. E. (1953), Clay Mineralogy: McGraw-Hill, 384 p.

GRUNER, J. W. (1934), The structures of vermiculites and their collapse by dehydration: *Am. Mineral*, **19**, 557–575.

HADLEY, J. B. (1949), Preliminary report on corundum deposits in Buck Creek peridotite, Clay County, North Carolina: *U. S. Geol. Surv. Bull.* **948-E**, 103–128.

HAGNER, A. F. (1944), Wyoming Vermiculite Deposits: *Univ. of Wyoming Geol. Surv. Bull.* **34**, 47 p.

KRIEGEL, W. W. (1940), Summary of occurrence, properties, and uses of vermiculite at Libby, Montana: *Am. Ceram. Soc. Bull.* **19**, 94–97.

KULP, J. L. AND BROBST, D. A. (1954), Notes on the dunite and the geochemistry of vermiculite at the Day Book dunite deposit, Yancey County, North Carolina: *Econ. Geol.*, **49**, 211–220.

MACKENZIE, R. C. (1957), The Differential Thermal Investigation of Clays: Mineralogical Soc. of London, 456 p.

PARDEE, J. J. AND LARSEN, E. S. (1929), Deposits of vermiculite and other minerals in the Rainy Creek district near Libby, Montana: *U. S. Geol. Surv. Bull* **805-B**, 13 p.

ROY, R. AND ROMO, L. A. (1957), Weathering studies. 1. New data on vermiculite: *Jour. of Geol.*, **65**, 603–610.

WEAVER, C. E. (1956), The distribution and identification of mixed-layer clays in sedimentary rocks: *Am. Mineral.*, **41**, 202–221.

ZONOLITE COMPANY (1954), Vermiculite, Chemical and Physical Properties: Company Publication G-81, 15 p.